A FUNDAMENTAL INVESTIGATION OF THE SYNTHESIS AND CHARACTERIZATION OF UCL_3 AND $(NH_4)_2UCL_6$ FOR APPLICATIONS OF TRANSURANIC CHLORIDE SYNTHESIS AND CHARACTERIZATION

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Overview

- Introduction
- Equipment
- Procedure
- $(NH_4)_2UCl_6$ Characterization
- UCl_3 Characterization
- Future Work
- Conclusions

Phase Equilibria in Systems Relevant to Pyroprocessing

- During electrorefining, contaminants less noble than uranium and transuranics anodically dissolve in electrolyte
  - Lanthanides, alkali and alkaline earth fission products
- There is a buildup of active metal and lanthanide fission products in the molten salt electrolyte
- The LiCl-KCl-TRUCl_3 system affects the thermodynamic activity of the chlorides, which affects the TRU-lanthanide separation factor
- $NpCl_3$ will be the first TRU chloride we investigate in the LiCl-KCl system
- $NpCl_3$ is not readily available and must be synthesized for use in the phase equilibria study

Need for Anhydrous Chloride Synthesis

- Numerous methods of synthesis for actinides tri- and tetrachloride
  - Dangerous bi-products
    - $AnO_{2\,(s)} + 2CCl_{4\,(g)} + Cl_{2\,(g)} \rightarrow AnCl_{4\,(s)} + \mathbf{2COCl_{2\,(g)}}$
  - Extremely high temperatures
    - Carbothermic reduction of AnO_2 to produce AnN
  - Expensive reagents
    - $AnN_{(s)} + 3Pt_{(s)} \rightarrow AnPt_{3(s)} + ½\ N_{2(g)}$
  - Residual contaminants
    - $AnO_{2(s)} + ¾\ ZrCl_4(LiCl\text{-}KCl)_{(l)} + ¼\ Zr_{(s)} \rightarrow AnCl_3(LiCl\text{-}KCl)_{(l)} + ZrO_{2(s)}$
  - Explosive hazards
    - $AnCl_{4(s)} + ½\ H_{2(g)} \rightarrow AnCl_{3(s)} + HCl_{(g)}$

Synthetic Approach

- **An or AnO_2 with NH_4Cl**
  - Well-known way of producing anhydrous rare earth chlorides
  - Previously used for UCl_4 and $PuCl_3$ synthesis
- Favorable synthetic conditions
  - Low temperature
    - 350 – 450 °C
  - Inexpensive reagents
  - No contaminants left in product
    - Such as ZrO_2
  - No dangerous bi-products
    - $HCl_{(g)}$ is evacuated from the chamber and scrubbed

Reaction with Actinide Oxides

1. $AnO_{2(s)} + 6\ NH_4Cl_{(s)} \rightarrow (NH_4)_2AnCl_{6(s)} + 2H_2O_{(g)} + 4\ NH_{3(g)}$

2. $(NH_4)_2AnCl_{6(s)} \rightarrow AnCl_{4(s)} + 2\ NH_{3(g)} + 2\ HCl_{(g)}$

3. $AnCl_{4(s)} + Zn_{(s)} \rightarrow AnCl_{3(s)} + ZnCl_{(s)}$

Reaction with Actinide Metal

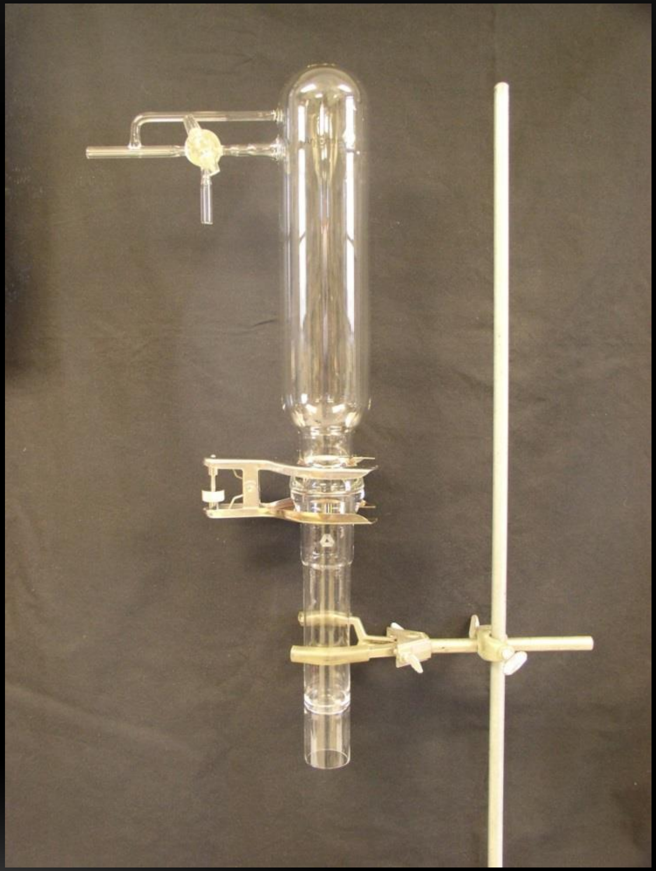
1. $An_{(s)} + 6\ NH_4Cl_{(s)} \rightarrow (NH_4)_2AnCl_{6(s)} + 4\ NH_{3(g)} + 2\ H_{2(g)}$

2.
   a) $(NH_4)_2AnCl_{6(s)} \rightarrow AnCl_{4(s)} + 2\ NH_{3(g)} + 2\ HCl_{(g)}$
   b) $(NH_4)_2AnCl_{6(s)} \rightarrow AnCl_{3(s)} + 2\ NH_{3(g)} + 2\ HCl_{(g)} + Cl_{2(g)}$

3. $3\ AnCl_{4(s)} + An_{(s)} \rightarrow 4\ AnCl_{3(s)}$

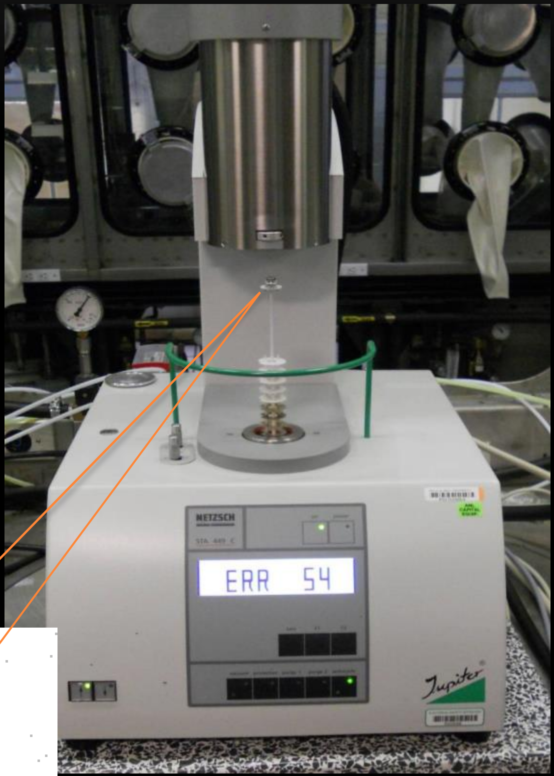
Equipment

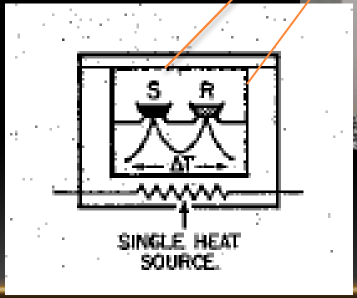
- Quartz reaction vessel
- Pyrex top sealed with O-ring
- Argon glove box
- Tube furnace with variac controller
- Small scale:
  - Pyrex reaction vessel
  - Pyrex top sealed with O-ring
- Reagents
  - Uranium dendrites
  - Anhydrous ammonium chloride



Standard Thermal Analyzer

- Combines thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)
- DSC
  - Identifies onset temperatures of phase transitions and enthalpy of the transitions
- TGA
  - Determines mass loss from the sample





Netzsch STA Jupiter 449C

Procedure

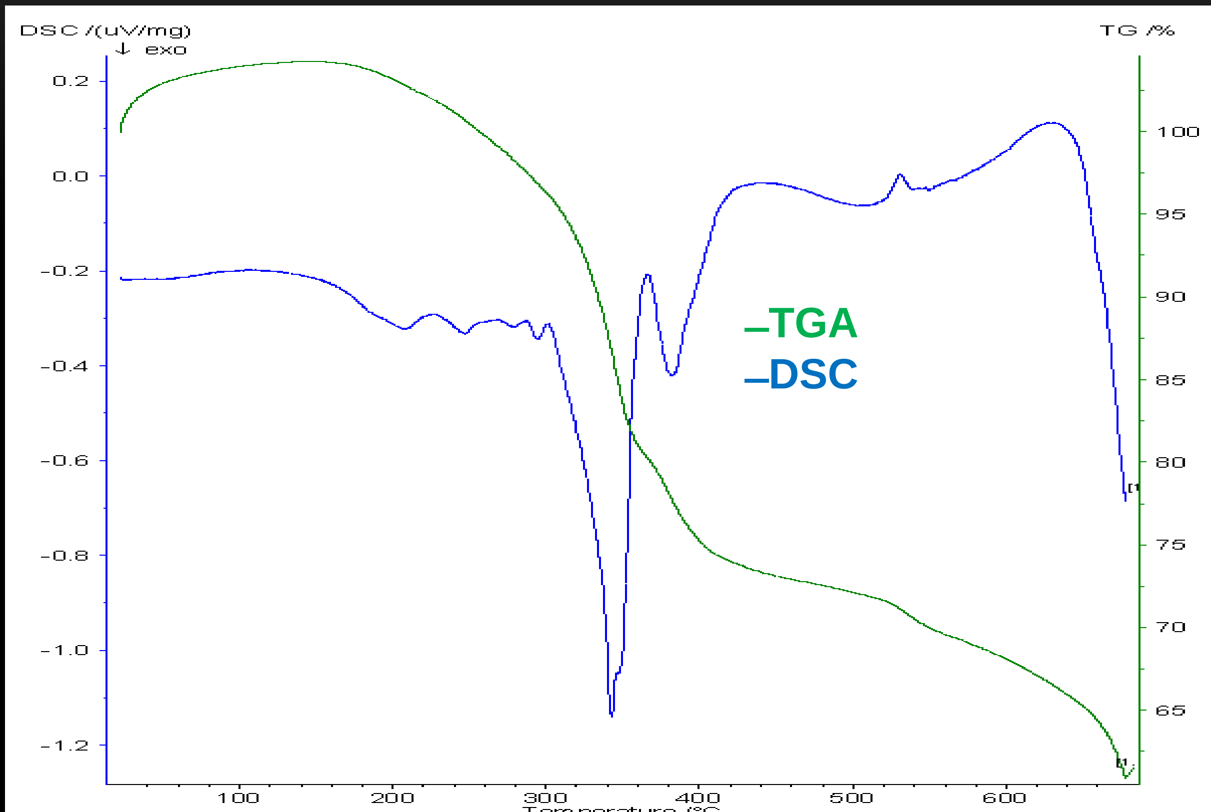
Product	Temperature (°C)	Hold Time (h)	Notes
$(NH_4)_2UCl_6$	300	30	
UCl_4	350	10	Vacuum
UCl_3	450	36	Vacuum

$(NH_4)_2UCl_6$
Intermediate Product

UCl_4 Product

UCl_3 Product

$(NH_4)_2UCl_6$ Results

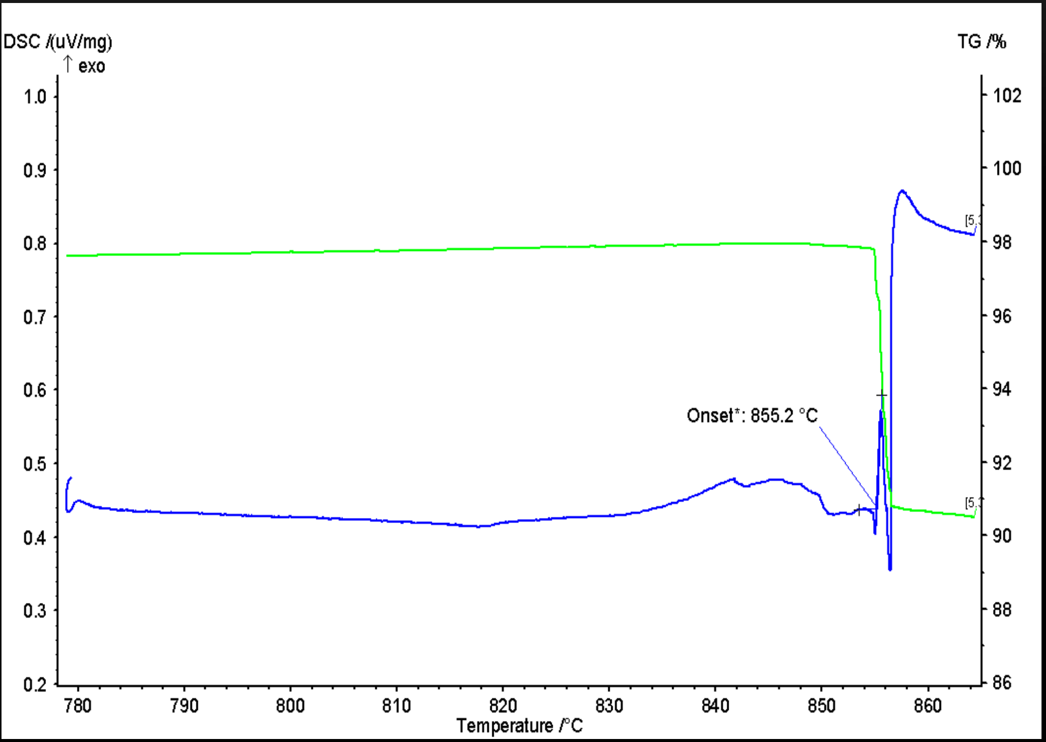


Decomposition of the intermediate occurs at 335 °C

Temperature Intervals (°C)	23-255	255-335	335-590	590-675
Weight Loss Expected (%)	0	11	22	-
Weight Loss Observed (%)	0	10.30	21.19	6.82

Second Heating Cycle of UCl_3

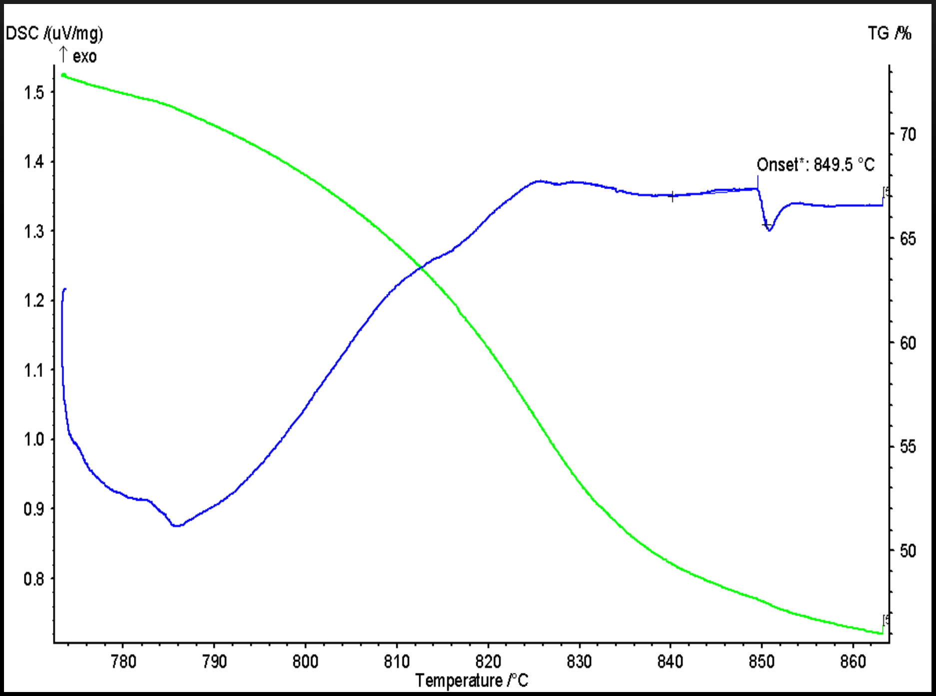
- Onset transition temperature of 855 °C corresponding to UCl_3 melting
- UCl_3 disproportionates upon melting:
  - $4\ UCl_3 \rightarrow U + 3UCl_4$
- TGA shows major mass loss upon melting corresponding to the UCl_4 sublimation
- DSC signal for cooling (not shown) displays small transition around 833 °C which might correspond to residual UCl_3



DSC and TGA in inert atmosphere DSC (blue) TGA (green)

Third Heating Cycle of UCl_3

- Onset transition temperature of 849 °C corresponding to UCl_3 melting
  - Much smaller transition due to smaller amount of UCl_3 in sample
- TGA signal stabilizes after final melting due to the complete sublimation of UCl_4
- DSC signal for cooling (not shown) does not display any additional transitions because UCl_3 completely disproportionated to UCl_4 and U



DSC and TGA in inert atmosphere DSC: blue, TGA: green.

FUTURE WORK

- Further Analysis of UCl_3 and $(NH_4)_2UCl_6$
  - Chemical analysis
  - XRD
- Synthesis of $NpCl_4$ and $NpCl_3$
- Synthesis of $AmCl_3$
- Phase investigation of $NpCl_4$ and $NpCl_3$ in the LiCl-KCl system

CONCLUSIONS

- Insight into chemistry gained during process feasibility tests
  - Verified the existence of $(NH_4)_2UCl_6$
  - $(NH_4)_2UCl_6$ decomposes to UCl_4 at 355 °C
  - Confirmed UCl_3 product
- Synthesis expected to be successful for TRU

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